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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 603 697 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 93120051.3

(22) Date of filing: 13.12.93

(51) Int. Cl.5: C04B 41/46, C07F 9/09, C08G 65/32

(30) Priority: 16.12.92 IT MI922860

(43) Date of publication of application: 29.06.94 Bulletin 94/26

(84) Designated Contracting States: AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

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(54) Process for imparting oil- and water-repellency to the surface of porous ceramic materials.

(57) Oil- and water-repellency is imparted to the surface of a porous ceramic material, in particular of "cotto", by applying a phosphoric monoester having formula:

$$[R_f\text{-O-CFY-L-O}]_m \overset{\overset{\displaystyle O}{\|}}{P} (O^-Z^+)_{3-m}$$

where:
L is a divalent organic group; m = 1; Y is -F or -CF_3; Z^+ is a cation; R_f is a polyperfluoroalkylene oxide chain.

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The present invention relates to a process for imparting oil- and water-repellency to the surfaces of porous ceramic materials and in particular of "cotto".

In the building industry, a broad use is made of porous ceramic materials, which exhibit a dull and rather irregular surface, because after baking they were not subjected to vitrification and/or enamelling treatments. A typical example is the so-called "Tuscan cotto", which is generally utilized as flooring material. It is a ceramic obtained by baking in an oven a mixing of clayish materials mainly composed of ores based on alumino-silicates, such as illite, illite-smectite, kaolinite, clorite, etc.

The porosity and the colour, which are typical of this type of ceramics, are highly appreciated for aesthetical reasons, but they involve considerable difficulties as regards cleaning. In fact dirtness, which can be carried by water or by oily substances, is easily absorbed and retained in the material pores, thereby causing a color alteration, and it is difficult to be removed by means of conventional washing techniques. The application of hydrocarbon-based waxes gives quite unsatisfactory results, as such products, although imparting an excellent water-repellency, exhibit a great affinity for oily products, wherefore, instead of repelling the fatty substances, favour the absorption of same.

It is known to use polyperfluoroalkylene oxides having perfluoroalkyl end groups for the protection of marble, stones, tiles, concrete and similar materials from the action of polluting atmospheric agents (see for example U.S. patent 4,499,146). Such products, besides imparting water- and oil-repellency properties, are endowed with a high permeability to gases and vapors, wherefore they permit to the protected material to "breathe". Furthermore, thanks to a very low refraction index, the polyperfluoroalkylene oxides do not alter the aspect and original color of the material, since optical interference and/or reflection phenomena do not occur.

The presence of porosity in the material to be protected leads to migration phenomena of the polyperfluoroalkylene oxides from the surface to the interior of the material, with consequent decrease of the protective action in the course of time. A considerable improvement with respect to U.S. patent 4,499,146 is represented therefore by the use of perfluoroalkylene oxides functionalized with groups, which are capable of fixing the product to the substrate to be protected, such as carboxylic, estereal, amidic, hydroxylic, isocyanic, epoxy, silanic etc. groups, as is described in U.S. patents 4.745,009 and 4,746,350. Many other functionalized polyperfluoroalkylene oxides are described in U.S. patent 4,085,137.

On the basis of the tests carried out by the Applicant, most of the products described in the above-cited patents are not suited to solve the technical problem underlaying the present invention, i.e. to provide products which are capable of:

(a) imparting a higher water- and oil-repellency to the surface of porous ceramic materials, and in particular to the surface of "cotto";

(b) remaining anchored to the surface of the treated material for a long time, in order not to cause migration to the interior of the same material and to withstand repeated washings with usual cleaners;

(c) not modifying the aesthetical characteristics of the treated material, in particular the color;

(d) being permeable to gases and vapors, in particular to water vapor;

(e) being applicable with economic methods, easy to be carried into pratice.

The Applicant has now surprisingly found that the phosphoric monoesters derived from polyperfluoroalkylene oxides fully meet the above-listed requirements.

Thus, it is an object of the present invention to provide a process for imparting oil- and water-repellency to the surface of a porous ceramic material, which process comprises applying onto said surface, a phosphoric monoester having the formula:

$$[R_f\text{-O-CFY-L-O}]_m\overset{\overset{\displaystyle O}{\|}}{P}\,(O^-Z^+)_{3-m} \qquad (I)$$

where:

L is a divalent organic group; m = 1; Y is -F or $-CF_3$; Z^+ is selected from: H^+; M^+ where M is an alkalimetal; $N(R)_4{}^+$ where groups R, like or different from ach other, are H or C_1-C_6 alkyls; R_f is a polperfluoroalkylene oxide chain.

A further object of the present invention are the phosphoric monoesters having formula (I) and the process for preparing them.

According to the process of the present invention, the phosphoric monomester of formula (I) can be optionally mixed with a phosphoric diester, corresponding to formula (I) where m = 2, and/or a phosphoric

triester, corresponding to formula (I), where $m = 3$, in such amounts that the monoester content is at least equal to 80 mols-%.

By L is meant a divalent organic group, preferably non-fluorinated, which can be selected from:

(a) $-CH_2-(OCH_2CH_2)_n-$, where n is an integer from 0 to 3;

(b) $-CO-NR'-(CH_2)_q-$, where R' is H or a C_1-C_4 alkyl; q is an integer from 1 to 4.

Groups R_f have preferably a number average molecular weight Mn ranging from 250 to 3,000, preferably from 400 to 1,000, and are composed of one or more repeating units randomly distributed along the chain and selected from:

(C_3F_6O); (C_2F_4O); $(CFXO)$, where X is -F or $-CF_3$;

$(CYZ-CF_2CF_2O)$, where Y and Z, like or different from each other, are F, Cl or H.

Poly-perfluoroalkylene oxide chains R_f can be selected in particular from the following classes:

(a)

$$T-O-(CF_2CF(CF_3)O)_m(CFXO)_n-CFZ- \quad (II)$$

where:

T is a (per)fluoroalkyl group selected from:

$-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$; X is -F or $-CF_3$; Z is -F, -Cl or $-CF_3$; m and n are numbers such that the n/m ranges from 0.01 to 0.5 and the molecular weight is in the above-indicated range;

(b)

$$T^{I}-O-(CF_2CF_2O)_p(CF_2O)_q-CFZ^{I}- \quad (III)$$

where:

T^{I} is a (per)fluoroalkyl group selected from:

$-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-C_2F_4Cl$; Z^{I} is -F or -Cl; p and q are numbers such that the q/p ratio ranges from 0.5 to 2 and the molecular weight is in the above indicated range;

(c)

$$T^{II}-O-(CF_2CF(CF_3)O)_r-(CF_2CF_2O)_s-(CFX^{II}O)_t-CFZ^{II}- \quad (IV)$$

where:

T^{II} is a (per)fluoroalkyl group selected from:

$-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$; X^{II} is -F or $-CF_3$; Z^{II} is -F, -Cl or $-CF_3$; r, s and t are numbers such that $r + s$ ranges from 1 to 50, the $t/(r+s)$ ratio ranges from 0.01 to 0.05 and the molecular weight is in the above indicated range;

(d)

$$T^{III}-O-(CF(CF_3)CF_2O)_u-CF(CF_3)- \quad (V)$$

where:

T^{III} is $-C_2F_5$ or $-C_3F_7$; u is a number such that the molecular weight is in the above indicated range;

(e)

$$T^{IV}-O-(CYZ-CF_2CF_2O)_v-CYZ-CF_2- \quad (VI)$$

where:

Y and Z, like or different from each other, are F, Cl or H; T^{IV} is $-CF_3$, $-C_2F_5$ or $-C_3F_7$; v is a number such that the molecular weight is in the above indicated range;

(f)

$$T^{V}-O-(CF_2CF_2O)_w-CF_2- \quad (VII)$$

where:

T^{V} is $-CF_3$ or $-C_2F_5$; w is a number such that the molecular weight is in the above indicated range.

The phosphoric monoester of formula (I) can be utilized either in acid form ($Z = H^+$), or salified with an alkaline metal hydroxide ($Z = M^+$, where M = Li, Na, K, etc.), or with ammonia or with an amine ($Z = N(R)_4^+$). Groups R can be optionaly substituted by hydroxyls or they can be linked to one another so as to form

a ring on the nitrogen atom, for example of the morpholinic type.

The amount of phosphoric monoester of formula (I) to be utilized in order to obtain an effective water- and oil-repellency action varies over a very wide range as a function of the surface characteristics of the material to be treated and of the molecular weight of the monoester itself. For example, for a typical "Tuscan cotto" there are applicable about 0.5 mg/cm^2 of a product of formla (I) having a R_f chain with Mn = 700. As a function of the specific conditions, for those skilled in the art it is sufficient to carry out a few tests for determining the optimum amount to be applied.

The monoester of formula (I) is preferably applied in the form of solution, at concentrations generally ranging from 0.1 to 5% by weight, preferably from 0.5 to 2% by weight.

Suitable solvents, or mixtures of solvents, can be selected from the following classes: aliphatic alcohols having 1 to 4 carbon atoms, fluorocarbons and chlorofluorocarbons, optionally containing hydrogen, ketones and esters having 3 to 10 carbon atoms, methylchloroform, low molecular weight (generally from 400 to 1,000) polyperfluoroalkylene oxide having fluoroalkyl end groups, etc. It is possible to use also solvent/non-solvent mixtures such as, for example, ketone/water mixtures or alcohols/water mixtures in ratios ranging from 10:90 to 90:10 by volume, or also (chloro)fluorocarbons/dimethylformamide mixtures or methylchloroform/dimethylformamide mixtures in ratios ranging from 1:1 to 3:1 by volume.

The choice of the most suitable solvent depends on everal factors. First of all, the solvent must be capable of dissolving, in the desired concentration, the specific product of formula (I) which is to be utilized. To this end it is sufficient to carry out some solubility tests.

Furthermore, the solvent must quickly dry, leaving the treated surface free from halos. In order to check whether the selected solvent meets this requirement, the following test can be conducted. 20 ml of solvent are dropped onto a "Tuscan cotto" tile having a surface of 450 cm^2; two hours after the application, at room temperature (25 °C) the "cotto" surface must be dry and free from halos.

The solvent suitability shall be further checked by applying onto a "Tuscan cotto" test piece, a solution composed of the solvent to be tested and of the product of formula (I) to be utilized, at the desired concentration. The surface so treated is subjected to a water-repellency test according to the method described later on herein. The solvent is to be considered as suitable if a sphericity index ranging from A to C is obtained (see the scale reported later on herein) and no dark halo apears at the base of the water drop (which halo indicates the absorption begin) in the ten minutes following the deposition of the drop. This additional test in order to check the solvent suitability is particularly important when it is desired to utilize solvent/non-solvent mixtures. In these cases, in fact, the solvent could evaporate too soon as compared with the non-solvent, thereby causing a non-uniform distribution of the product on the treated surface.

The phosphoric monoesters of formula (I) are preparable by reacting the corresponding hydroxy-terminated polypefluoroalkylene oxides R_f-O-CFY-L-OH with $POCl_3$ in such molar ratios that $POCl_3$ is always in great excess. Generally, the $POCl_3$/hydroxy-terminated product molar ratio ranges from 5:1 to 10:1, preferably from 6:1 to 8:1. The reaction is conducted by gradually dropping the hydroxy-terminated product into $POCl_3$, in the presence of a base, for example a tertiary amine, such as pyridin, triethylamine, tributylamine, at a temperature generally ranging from 50° to 100°C, preferably from 70° to 90°C. The reaction is conducted, always under stirring, until disappearance of the hydroxylic groups, what can be checked by infrared analysis. The $POCl_3$ excess is removed by distillation and the resulting product is hydrolized with water or with diluted hydrochloric acid. The organic phase is separated by extraction with a proper water-insoluble solvent for example a (chloro)fluorocarbon or methylchloroform. The separation is preferably carried out in the presence of a co-solvent, for example a water-soluble ketone, which has the function of preventing the formation of emulsions, which would hinder the separation of the organic product. From the organic phase, the product is separated according to conventional techniques, such as, for example, evaporation of the solvent.

From such reaction, the monoesters are obtained with high yields, usualy in admixture with minor amounts of the corresponding di- and tri-esters.

The hydroxy-terminated polyperfluoroalkylene oxides R_f-O-CFY-L-OH are known products and are preparable according to known methods starting from the coresponding polyperfluoroalkylene oxides having -COF end groups. The starting polypefluoroalkylene oxides containing end groups -COF are described, for example, in patents: GB 1,104,482 (class (a)), US 3,715,378 (class (b)) , US 3,242,218 (class (c)) , US 3,242,218 (class (d)), EP 148,482 (class (e)), US 4,523,039 (class (f)), or also in patent application EP 340,740 and WO 90/03357.

In particular, products R_f-O-CFY-L-OH, where L = $-CH_2(OCH_2CH_2)_n-$ can be prepared by reduction of the corresponding fluorinated acids and, when n ≠ 0, by subsequent ethoxylation reaction with ethylene oxide, conforming to what is described, for example, in patents: US 3,293,306, US 3,847,978, US 3,810,874 and US 4,814,372.

The products where L = -CO-NR'-$(CH_2)_q$- are preparable by reacting the corresponding acyl fluorides with an alkanolamine of formula R'-NH-$(CH_2)_q$-OH.

The monophosphoric acids utilized in the process of the present invention, besides imparting a particularly high oil- and water-repellency degree, are also capable of stably anchoring to the substrate, wherefore no migration phenomena to the substrate interior have been observed. Furthermore, the treated surface retains the oil- and water-repellency characteristics even afterrepeated washings with the most common cleaners.

The present invention will be now described more in detail by the following examples, which are given merely for purposes of illustration and are not intended to limit the scope of the invention.

The oil- and water-repelency degrees have been determined by observing the behaviour of an oil drop or water drop deposit onto the treated surface, taking two distinct parameters into consideration: drop sphericity and absorption time.

The drop sphericity is in itself a measure of the liquid repellency, and it can be determined by measuring the contact angle, i.e. the angle formed by the substrate plane and by the tangent to the drop surface in the point of contact with said plane. A perfectly spheric drop has a contact angle of 180°, while a flat drop has a contact angle tending to 0°.

Due to the irregularity of the "Tuscan cotto" surface, an accurate measurement of the contact angle is practicaly impossible, wherefore to discrete intervals of contact angle, a sphericity index according to the following scale has been correlated:

Sphericity index	Contact angle
A	about 180°
B	150°-180°
C	120°-150°
D	90-120°
E	< 90°

A perfectly spheric drop, which has a practically punctiform contact surface has a sphericity index A; nearly perfectly spheric drops, having an extremely reduced, but not punctiform surface contact surface, have been classified with B; index C has been attributed to drops exhibiting a good sphericity, having a rather wide contact surface, but always smaller than the dimensions of the drop. At D and E, the contact angle furthery decreases and, correspondingly the contact surface increases. The values reported in the examples represent an average calculated on 20 drops, having a volume of about 3 µl and deposited onto 25 cm^2 of "Tuscan cotto". For the water-repellency test, demineralized water has been utilized, while for the oil-repellency test, a paraffin oil having a viscosity of 20 cSt (commercial product: ESSO P60®) was utilized.

A correct evaluation of the liquid-repellency degree must take another parameter into account, namely the complete absorption time of the drop by the treated material surface (hereinafter referred to as t). Of course, in the case of water (water-repellency), the drop volume decreases in the time also due to the evaporation, wherefore there is a maximum time limit, within which the evaluation is still possible. At room temperature for a water drop of 3 µl, a maximum limit of 30 minutes has been fixed. In the case of oil (oil-repellency), the evaporation is quite negligible, wherefore the maximum limit has been arbitrarily fixed at 7 days.

The begin of the absorption, if any, is indicated by the appearance of a dark halo at the drop base, which halo extends in the course of time and is accompanied by a proportional reduction of the drop volume.

The evaluation scale of the absorption index has been fixed as follows:

Absorption index	t	
	Water (min.)	Oil (hours)
a	0	0
b	2.5	1
c	5	2
d	10	3
e	15	4
f	20	5
g	25	6
h	30	24
i	--(*)	--(*)

(*) absence of absorption

Both for the water-repellency and for the oil-repellency, the dark halo appears within 5 minutes after the drop deposition at absorption indexes from (a) to (d), within 10 minutes at indexes from (e) to (h). No halo appears at absorption index (i).

In like manner as for the sphericity index, the values reported in the examples are the average calculated on 20 drops having a volume of about 3 μl and deposited on 25 cm^2 of "Tuscan cotto".

On the basis of the sphericity index and absorption index determined according to the criteria described hereinabove, the following evaluation scale has been fixed, which is valid for both the oil-repellency and the water-repellency:

Oil- or water-repellency	Sphericity index	Absorption index
0	E	a
1	E	b
2	E	c
3	E	d
4	E	e
5	E	f
6	E	g
7	D	h
8*	E	i
8	C	i
9	B	i
10	A	i

EXAMPLE 1

Onto a "Tuscan cotto" tiles measuring 5 x 5 cm it was dropped 1 ml of solution, at 1% by weight in isopropanol, of a mixture consisting for 90 mols-% of a phosphoric monoester coresponding to formula (I) with:

L = $-CH_2(OCH_2CH_2)-$; m = 1; Z^+ = H^+; R_f is a chain of Galden® Y (formula (II)), having Mn = 700,

Mw/Mn = 1.3, m/n = 20. The remaining 10% consisted of a mixture of the corresponding diester (m = 2) and triester (m = 3).

The "cotto" was allowed to dry at room temperature for 2 hours. Then the water- and oil-repellency was evaluated conforming to the method described hereinbefore. The values are reported intable I.

The applied prodct was obtained as follows. 200 g (0.277 mols) of the corresponding hydroxy-terminated Galden® Y were gradually dropped (in 4 hours) into 225 g of $POCl_3$ ($POCl_3$/Galden molar ratio = 6:1). The reaction was maintained under stirring for one hour more. During all the reaction time, the temperature was maintained at 90 °C. The $POCl_3$ excess was then distilled off (at 50 °C/20 mmHg). The distillation residue was then hydrolized by addition of 60 ml of H_2O. After addition of 90 ml of A113 (CF_2Cl-$CFCl_2$) and of 35 ml of acetone, the organic phase was separated in an extraction funnel. The product contained in the organic phase was dried by evaporation of the solvents (at 80 °C/1 mbar). There were obtained 192 g of a product consisting for 90 mols-% of monoester and for 10 mols-% of di- and tri-ester, as it was checked by acidimetric titration and ^{31}P-NMR analysis.

EXAMPLES 2-3

Example 1 was repeated under the same conditions and with the same product utilizing solutions in isopropanol at 2.5% by weight (Ex. 2) and at 5.0% by weight (Ex. 3). The oil- and water-repellency values are reported in Table I.

EXAMPLES 4-6

Examle 1 was repeated under the same conditions and with the same product, using as a solvent an isopropanol/water mixture in a 20:80 ratio by volume. Solutions at a concentration of 1.0% (Ex. 4), 2.5% (Ex. 5) and 5.0% (Ex. 6) by weight were applied. The water- and oil-repellency values are reported in Table I.

EXAMPLES 7-8

Example 1 was repeated under the same conditions and with the same product, utilizing as a solvent an isopropanol/water mixture in a 50:50 ratio by volume. Solutions at a concentration of 2.5% (Ex. 7) and 5.0% (Ex. 8) by weight were applied. The water- and oil-repellency values are reported in table I.

EXAMPLES 9-10

Example 1 was repeated under the same conditions and with the same product, utilizing as a solvent a water/glycol/isopropanol mixture in a 69:17:14 ratio by volume. Solutions at a concentration of 2.5% (Ex. 9) and 5.0% (Ex. 10) by weight were applied. The water- and oil-repellency values are reported in Table I.

EXAMPLES 11-12

Example 1 was repeated under the same conditions and with the same product, using as a solvent a water/glycol/isopropanol mixture n a 75:8:17 ratio by volume. Solutions at a concentration of 2.5% (Ex. 11) and 5.0% (Ex. 12) by weight were applied. The water- and oil-repellency values are reported in Table I.

EXAMPLE 13

Example 1 was repeated utilizing a solution, at 1% by weight in isopropanol, of a mixture composed for 90 mols-% of a phosphoric monoester corresponding to formula (I) where: L = $-CH_2(OCH_2CH_2)-$; m = 1; Z^+ = H^+; R_f is a chain of Galden® Y (formula (II)), having Mn = 900, Mw/Mn = 1.0, m/n = 20. The remaining 10% was composed of the corresponding diester (m = 2) and triester (m = 3). The product was prepared according to the same method described in Example 1. The water- and oil-repellency values are reported in table II.

EXAMPLES 14-15

Example 1 was repeated utilizing solutions, at 0.5% (Ex. 14) and 1.0% (Ex. 15) by weight in isopropanol, of a mixture composed for 90 mols-% of a phosphoric monoester corresponding to formula (I) where: L = $-CH_2(OCH_2CH_2)-$; m = 1; Z^+ = H^+; R_f is a chain of Galden® Y (formula (II)), having Mn = 400,

Mw/Mn = 1.0, m/n = 20. The remaining 10% consisted of the corresponding diester (m = 2) and triester (m = 3). The product was prepared according to the same method described in Example 1. The water- and oil-repellency values are reported in Tabel II.

EXAMPLE 16

The phosphoric monoester of example 13 was salified with a hydroalcoholic KOH solution in a stoichiometric amount. After removal of the solvent by evaporation, the product was dissolved in A113 in such amount as to obtain a solution at 1% by weight. Such solution was applied on a "Tuscan cotto" according to the modalities described in Example 1. The water- and oil-repellency values are reported in table II.

EXAMPLE 17 (comparative)

Example 1 was repeated utilizing a solution, at 1% by weight in isopropanol, of a product of formula:

$$R_f\text{-}CF_2\text{-}CH_2(OCH_2CH_2)O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_2\text{-}Pi^+\ Cl^-$$

where Pi is a pyridinic ring, R_f is a chain of Galden® Y (formula (II)), with Mn = 700 and Mw/Mn = 1.3 and m/n = 20.

Such product was obtained - according to what is described in Italian patent application No. 360/MI92A, filed on February 20, 1992 by the Applicant - by esterification reaction of the hydroxy-derivative of formula: R_f-CF_2-$CH_2(OCH_2CH_2)OH$ with chloroacetic acid, and subsequent quaternization with pyridin in isopropanol.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 18 (comparative)

Example 1 was repeated utilizing a solution of 5% by weight in A113 of a mixture composed of R_f-COO^-TEA^+ (TEA = triethanolamine) and of the corresponding ketone R_f-CO-CF_3, in a 1:2 molar ratio, where R_f is a chain of Galden® Y (formula (II)), having Mn = 2,700, Mw/Mn = 1.3 and m/n = 35. Such mixture was obtained, according to conventional techniques, by acid hydrolysis and subsequent salification with TEA of the product deriving from the thermal treatment (200-250°C) of the rough product resulting from the photooxidation of hexafluoropropene with O_2.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 19 (comparative)

Example 1 was repeated using a solution at 1% by weight in isopropanol of a product of formula:

R_f-CO-NH-$(CH_2)_3$-$Si(OC_2H_5)_3$

where R_f is a chain of Galden® Y (formula (II)), having Mn = 700, Mw/Mn = 1.3 and m/n = 20. Such product was obtained by reating the corresponding acyl-derivative with 3-amino-propyl-triethoxysilane.

The water- and oil-repellency values are reported in table III.

EXAMPLE 20 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a non-functionalized Galden® Y, corresponding to formula (II) with CF_3 end group, having Mn = 1,500, obtained via functional distillation of the corresponding commercial product.

The water- and oil-repellency vaues are reported in table III.

EXAMPLE 21 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a product of formula:

$R_f\text{-}CF_2(OCH_2CH_2)_6\text{-}OH$

where R_f is a chain of Galden® Y (formula (II)), having Mn = 700, Mw/Mn = 1.3 and m/n = 20. Such product was obtained by reduction of the corresponding Galden® Y having -COF end groups and by subsequent ethoxylation with ethylene oxide.

The water- and oil-repellency values are reported in table III.

EXAMPLE 22 (comparative)

Example 1 was repeated utilizing a solution at 4% by weight in A113 of a product of formla:

$R_f\text{-}CO\text{-}OH$

in admixture with a ketone of formula:

$R_f\text{-}CO\text{-}CF_3$

where R_f is a chain of Galden® Y (formula (II)), having Mn = 2,700, Mn/Mw = 1.3 and m/n = 35. The acid/ketone molar ratio of about 1:2. It was the same product utilized in Example 18, but not subjected to salifiction with TEA.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 23 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a product of formula:

$R_f\text{-}COOH$

where R_f is a chain of Galden® Y (formula (II)), having Mn = 700, Mw/Mn = 1.3 and m/n = 20. Such product was obtained by hydrolysis of the corresponding Galden® Y having -COF end groups.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 24 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight of A113 of a product of formula:

$R_f\text{-}COOH$

where R_f is a chain of Galden® Y (formula (II)), having Mn = 2,700, Mw/Mn = 1.3 and m/n = 35, obtained from the product utilized in Example 22 by selective precipitation of the acids as calcium salts and by subsequent acidification.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 25 (cmparative)

Example 1 was repeated utilizing a slution at 1% by weight in A113 of product of formula:

$R_f\text{-}CH_2OH$

where R_f is a chain of Galden® Y (formula (II)), having Mn = 700, Mw/Mn = 1.3 and m/n = 20. Such product was obtained by reduction of the corresponding Galden$^{(R)}$ Y having -COF end groups.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 26 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a product of formula:

R_f-$CH_2OCH_2CH_2$-OH

where R_f is a chain of Galden(R) Y (formula (II)), having Mn = 700, Mw/Mn = 1.3 and m/n = 20. Such product was obtained by reduction of the corresponding Galden (R) Y having -COF end groups and by subsequent ethoxylation with ethylene oxide.

The water- and oil-repellency values are reported in Table III.

EXAMPLE 27 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in water of Surflon(R) S-112 (salified perfluoroalkyl phosphate) produced by Asahi Glass Co..

The water- and oil-repellency values are reported in Table III.

TABLE I

EX.	SOLVENT	CONC. (% by wg.)	WATER-REPELLENCY	OIL-REPELLENCY
1	isopropanol	1.0	8	8
2	"	2.5	8	8
3	"	5.0	8	8
4	isoprop./H_2O 20/80	1.0	9	8
5	"	2.5	9	8
6	"	5.0	9	8
7	isoprop./H_2O 50/50	2.5	8	8
8	"	5.0	9	8
9	H_2O/glycol/isoprop. 69/17/14	2.5	8	8
10	"	5.0	8	8
11	H_2O/glycol/isoprop. 75/8/17	2.5	8	8
12	"	5.0	8	8

TABLE II

EX.	SOLVENT	CONC. (% by wg.)	WATER-REPELLENCY	OIL-REPELLENCY
13	isopropanol	1.0	9	8
14	"	0.5	8	8
15	"	1.0	8	8
16	A113	1.0	9	8

TABLE III

(Comparative Examples)			
EX.	PRODUCT	WATER-REPELLENCY	OIL-REPELLENCY
17	$R_fCF_2CH_2OCH_2CH_2O$-CO-CH_2-Pi^+Cl^-	0	7
18	R_f-COO^-TEA^+ + R_f-CO-CF_3	2	7
19	R_f-CO-NH-$(CH_2)_3$-Si $(OC_2H_5)_3$	0	3
20	R_f-CF_3	0	0
21	R_f-$CH_2(OCH_2CH_2)_6$-OH	0	7
22	R_f-CO-OH + R_f-CO-CF_3	0	3
23	R_f-COOH	0	6
24	R_f-COOH	0	8*
25	R_f-CH_2OH	0	6/7
26	R_f-$CH_2OCH_2CH_2$-OH	0	8*
27	$(C_nF_{2n+1})_m$-PO- $(O^-Z^+)_{3-m}$	2	8

Claims

1. A process for imparting oil- and water-repellency to the surface of a porous ceramic material, which comprises applying onto said surface a phosphoric monoester of formula:

$$[R_f\text{-O-CFY-L-O}]_m\overset{\displaystyle O}{\overset{\|}{P}}(O^-Z^+)_{3-m} \qquad (I)$$

where:
L is a divalent organic group; m = 1; Y is -F or -CF_3;
Z^+ is selected from: H^+; M^+ where M is an alkaline metal;
$N(R)_4{}^+$ where groups R, like or different from one another, are H or C_1-C_6 alkyls; R_f is a polyperfluoroalkylene oxide chain.

2. The process of claim 1, wherein the phosphoric monoester of formula (I) is mixed with a phosphoric diester, corresponding to formula (I) where m = 2, and/or a phosphoric triester, corresponding to formula (I) where m = 3, in such amounts that the monoester content is at least equal to 80 mols-%.

3. The process of any of the preceding claims, wherein group L is selected from:
   (a) -CH_2-$(OCH_2CH_2)_n$-, where n is an integer ranging from 0 to 3;
   (b) -CO-NR'-$(CH_2)_q$-, where R' is H or a C_1-C_4 alkyl; q is an integer ranging from 1 to 4.

4. The process of any of the preceding claims, wherein the R_f chains are composed of one or more repeating units, statistically distributed along the chain, selected from: (C_3F_6O); (C_2F_4O), (CFXO), where X is -F or -CF_3; (CYZ-CF_2CF_2O), where Y and Z, like or different from each other, are F, Cl or H, and have a number average molecular weight ranging from 350 to 3,000.

5. The process of claim 4, wherein the R_f chains have a number average molecular weight ranging from 400 to 1,000.

6. The process of claim 4 or 5, wherein the R_f chains are selected from the following classes:

(a)

$T\text{-}O\text{-}(CF_2CF(CF_3)O)_m(CFXO)_n\text{-}CFZ\text{-}$ (II)

where:
T is a (per)fluoroalkyl group selected from:
$-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$; X is -F or $-CF_3$; Z is -F, -Cl or $-CF_3$; m and n are numbers such that the n/m ratio ranges from 0.01 to 0.5 and the molecular weight is in the above-indicated range;
(b)

$T^{I}\text{-}O\text{-}(CF_2CF_2O)_p(CF_2O)_q\text{-}CFZ^{I}\text{-}$ (III)

where:
T^{I} is a (per)fluoroalkyl group selected from:
$-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-C_2F_4Cl$; Z^{I} is -F or -Cl, p and q are numbers such that the q/p ratio ranges from 0.5 to 2 and the molecular weight is in the above indicated range;
(c)

$T^{II}\text{-}O\text{-}(CF_2CF(CF_3)O)_r\text{-}(CF_2CF_2O)_s\text{-}(CFX^{II}O)_t\text{-}CFZ^{II}\text{-}$ (IV)

where:
T^{II} is a (per)fluoroalkyl group selected from:
$-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$; X^{II} is -F or $-CF_3$; Z^{II} is -F, -Cl or $-CF_3$; s and t are numbers such that r + s ranges from 1 to 50, the t/(r+s) ratio ranges from 0.01 to 0.05 and the molecular weight is in the above indicated range;
(d)

$T^{III}\text{-}O\text{-}(CF(CF_3)CF_2O)_u\text{-}CF(CF_3)\text{-}$ (V)

where:
T^{III} is $-C_2F_5$ or $-C_3F_7$; u is a number such that the molecular weight is in the above indicated range;
(e)

$T^{IV}\text{-}O\text{-}(CYZ\text{-}CF_2CF_2O)_v\text{-}CYZ\text{-}CF_2\text{-}$ (VI)

where:
Y and Z, like or different from each other, are F, Cl or H; T^{IV} is $-CF_3$, $-C_2F_5$ or $-C_3F_7$; v is a number such that the molecular weight is in the above indicated range;
(f)

$T^{V}\text{-}O\text{-}(CF_2CF_2O)_w\text{-}CF_2\text{-}$ (VII)

where:
T^{V} is $-CF_3$ or $-C_2F_5$; w is a number such that the molecular weight is in the above indicated range.

7. The process of any of the preceding claims, wherein the phosphoric monoester is applied in the form of a solution at a concentration ranging from 0.1 to 5% by weight.

8. The process of claim 7, wherein the phosphoric monoester is applied in the form of a solution in a solvent selected from: aliphatic alcohols having 1 to 4 carbon atoms, fluorocarbons and chlorofluorocarbons optionally containing hydrogen, ketones and esters having 3 to 10 carbon atoms, methylchloroform, low molecular weight polyperfluoroalkylene oxides having fluoroalkyl end groups, or mixtures thereof.

9. The process of claim 7, wherein the phosphoric monoester is applied in the form of a solution in a solvent/non-solvent mixture selected from: ketone/water, alcohols/water, (chloro)-fluorocarbons/dimethylformamide, methylchloroform/dimethylformamide.

10. Phosphoric monoesters having formula:

$$[R_f\text{-O-CFY-L-O}]_m \overset{\displaystyle O}{\overset{\|}{P}} (O^-Z^+)_{3-m} \qquad (I)$$

as defined in claims 1 to 6.

11. The process for preparing the phosphoric monoesters of claim 10, which comprises reacting, in the presence of a base, the corresponding hydroxy-terminated polyperfluoroalkylene oxides R_f-O-CFY-L-OH with $POCl_3$, in such amount that the $POCl_3$/hydroxy-terminated product molar ratio ranges from 5:1 to 10:1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 12 0051

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
P,Y	DATABASE WPI Section Ch, Week 9312, Derwent Publications Ltd., London, GB; Class D21, AN 93-096729 & JP-A-5 039 209 (KAO CORP.) 19 February 1993 * abstract * ---	1,3-6, 10,11	C04B41/46 C07F9/09 C08G65/32
Y	US-A-3 188 340 (A. K. MACKENZIE)	1,3-6, 10,11	
A	* column 1, line 1 - column 2, line 59 * ---	8-11	
A	DATABASE WPI Section Ch, Week 9240, Derwent Publications Ltd., London, GB; Class D21, AN 92-3228086 & JP-A-4 235 908 (KAO CORP.) 25 August 1992 * abstract * ---	1,3,4,6, 10	
A	US-A-3 492 374 (R. E. LE BLEU ET AL) * column 1, line 15 - column 2, line 40 * * column 4, line 24 - column 6, line 9 * * claim 1; examples 8,9 * ---	1,3,4, 6-11	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C04B C07F C08G
A	DE-A-24 13 970 (DAIKIN KOGYO KK) * page 2, line 1 - page 3, line 20 * * page 5, line 30 - page 6, line 20; claim 1; example 1 * -----	1,3,4, 7-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 March 1994	Olsson-Norgren, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document